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Scalable, cost-efficient synthesis and properties optimization of magnetoelectric cobalt ferrite/barium titanate composites

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ABSTRACT

Cobalt ferrite (CoFe_2O_4)/barium titanate (BaTiO_3) particulate composites exhibiting high magnetoelectric coefficients were synthesized from low-cost commercial precursors using mechanical ball milling followed by high-temperature annealing. CoFe_2O_4 (20 nm–50 nm) and either cubic or tetragonal BaTiO_3 nanoparticle powders were used for the synthesis. It was found that utilizing a 50 nm cubic BaTiO_3 powder as a precursor results in a composite with a magnetoelectric coupling coefficient value as high as 4.3 mV/Oe cm, which is comparable to those of chemically synthesized core-shell CoFe_2O_4 - BaTiO_3 nanoparticles. The microstructure of these composites is dramatically different from the composite synthesized using 200 nm tetragonal BaTiO_3 powder. CoFe_2O_4 grains in the composite prepared using cubic BaTiO_3 powder are larger (by at least an order of magnitude) and significantly better electrically insulated from each other by the surrounding BaTiO_3 matrix, which results in a high electrical resistivity material. It is hypothesized that mechanical coupling between larger CoFe_2O_4 grains well embedded in a BaTiO_3 matrix in combination with high electrical resistivity of the material enhances the observed magnetoelectric effect.

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INTRODUCTION

Magnetoelectric (ME) effect^{1–5} has a number of promising applications in sensors, energy harvesting, magnetoelectric random access memory, antennas, drug delivery, etc.^{6,7} In ME materials, the electric polarization can be controlled by varying the material's magnetization state, and conversely, varying the electric polarization affects the material's magnetization state. The ME effect has been observed in a few single-phase *multiferroic* materials; however, the effect is relatively weak at room temperature, which hampers useful applications. More robust ME behavior has been achieved in composites that combine mechanically coupled magnetostrictive and piezoelectric materials arranged in a matrix.^{6,8} The ME effect in such composites is due to the induced stresses within the

magnetostrictive or piezoelectric phases controlled by the application of external magnetic or electric fields, which transfer through the interface to the piezoelectric or magnetostrictive phases, respectively.⁹ These composites can be produced in versatile connectivity configurations/matrices with a wide choice of materials, volume fractions, and microstructures^{8,10} and can exhibit several orders of magnitude stronger ME effect than single-phase ME materials. Composite ME materials have been synthesized using a variety of techniques including sol-gel electrospinning of nanofibers,⁹ polyol mediated process of composite ceramics,¹⁰ molten-salt synthesis route for bulk composites,¹¹ core-shell structures,^{12,13} wet ball-milling,¹⁴ one-pot process,¹⁵ carbon combustion synthesis,¹⁶ and feather-like nanostructures.¹⁷ The ME coefficient for these composites ranges from a few $\mu\text{V/Oe cm}$ to several mV/Oe cm .⁹ Core-shell

nanostructures, where the magnetostrictive core is fully enclosed by a piezoelectric shell, typically exhibit a higher value of ME coefficients. However, relatively complex chemical synthesis techniques along with the relatively low material yields limit their applications. Other synthesis approaches often suffer from poor interfaces between the two phases and/or low resistivity of magnetostrictive components, which hinders effective electrical poling.

In this study, the synthesis and characterization of CoFe_2O_4 - BaTiO_3 particulate composites using dry ball-milling followed by annealing as a simple, low-cost, and highly reproducible powder processing method are presented. Cobalt ferrite, CoFe_2O_4 , is a magnetostrictive material with magnetostriction coefficient values as high as 100 ppm–200 ppm at saturation,^{18–20} and the tetragonal phase of barium titanate, BaTiO_3 , is piezoelectric with reported d_{33} piezoelectric coefficient values in the 190 pC/N–260 pC/N range at room temperature.^{21–25} The overarching goal of this work is to develop a scalable synthesis of an ME composite utilizing readily available commercial CoFe_2O_4 (CFO) and BaTiO_3 (BTO) precursor nanopowders. While there are several published reports on CoFe_2O_4 - BaTiO_3 composites prepared by wet mechanical ball-milling, these reports have only partially explored the relationships between the process parameters and the properties of the composite.^{14,26,27} The structural, magnetic, and ME properties of CoFe_2O_4 - BaTiO_3 composites were investigated as functions of preparation conditions and the types of BaTiO_3 precursor nanoparticles used, namely, 50 nm cubic BaTiO_3 powder and 200 nm tetragonal BaTiO_3 powder. The ME coefficient in the optimized CoFe_2O_4 - BaTiO_3 composite, where individual CoFe_2O_4 grains are fully enclosed by the BaTiO_3 matrix, was found to be comparable with the numbers reported for the composites based on core-shell structures.^{28,29}

CoFe_2O_4 - BaTiO_3 composite synthesis and sample conditioning

A 99.9% purity cobalt ferrite powder with 20 nm–50 nm particle sizes and 99.9% purity cubic and tetragonal barium titanate powders with 50 nm and 200 nm average particle sizes, respectively, were used in this study (see Fig. 1).³⁰ The composite mixture [$x\text{-CoFe}_2\text{O}_4$ -(1 - x)- BaTiO_3 , where x is the weight fraction] was prepared using mechanical ball milling. The mixture of CoFe_2O_4 and BaTiO_3 powders was ball-milled using a high-speed vibrating milling machine (MTI Corporation MSK-SFM-3) at 288 rpm for

5 h in a dry medium. Ball milling was performed using a nylon jar filled with zirconia balls with a ball to powder mass ratio of 10:1. The resulting mixture was pressed into pellets with a diameter of ~12 mm and a thickness of ~1 mm using a hydraulic press at a pressure of 120 bars. Next, the pellets were sintered in air for 4 h at 1200 °C in a tube furnace (MTI Corporation OTF-1200X-S).

Tetragonal BaTiO_3 is piezoelectric, but cubic BaTiO_3 does not exhibit ferroelectric behavior due to its centrosymmetric crystal structure. However, cubic BaTiO_3 undergoes a structural transformation as it reaches certain critical temperatures. The most typical conversion from paraelectric cubic to ferroelectric tetragonal crystal structure occurs through cooling through its Curie point at 120 °C. This structural transformation is due to a slight displacement of Ti^{4+} cations with respect to the anion center along the crystallographic c axis.^{21–23}

The annealed pellets were electrically poled in the direction perpendicular to the pellet surface in a heated silicone oil bath at 150 °C, which is above the BaTiO_3 Curie temperature for 15 min. The poling voltage was maintained after the pellet was removed from the bath for an additional 15 min as the pellet cools down to room temperature. As discussed later, the magnitude of the poling voltage affects the measured ME properties.

Materials characterization

The magnetoelectric behavior was evaluated using a custom-built ME characterization system similar to the one described in the literature.^{31–33} The opposing surfaces of the samples were coated with a thin layer of conductive silver paste (MG chemicals 842-AR silver print) as the electrical contacts for magnetoelectric measurement. The ac ME voltage across the pellet induced by the ac magnetic field (1 Oe at 1 KHz) superimposed over a dc magnetic field is recorded as a function of dc magnetic field, which can be swept between -7 kOe and 7 kOe. Stimulating the sample with an ac magnetic field superimposed to the dc magnetic field eliminates the contribution of charges accumulated in the grain boundaries and defects in the material during the poling process into the ME signal.^{33–35} Piezo-force microscopy (PFM) measurements were performed utilizing an MFP-3D Origin+ (Asylum Research-Oxford Instruments) atomic force microscope in the Dual AC Resonance Tracking (DART) mode using a silicon tip coated with Ti/Ir (5/20). The microstructure was examined utilizing an FEI Dual Beam 235 Focused Ion Beam instrument. The magnetostriction

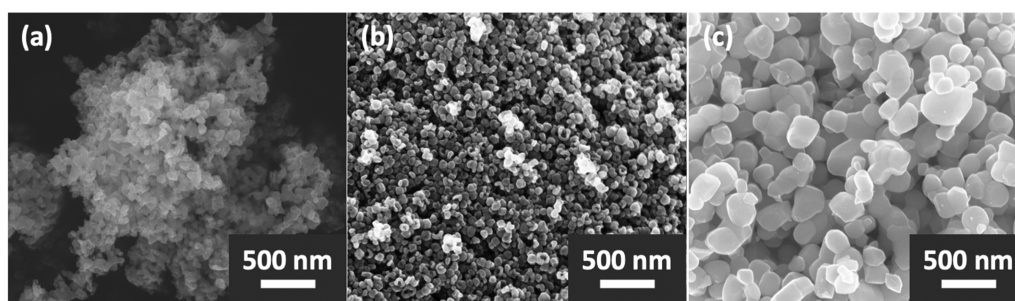


FIG. 1. SEM images of (a) 20 nm–50 nm CoFe_2O_4 , (b) 50 nm cubic BaTiO_3 , and (c) 200 nm tetragonal BaTiO_3 .

measurement was performed using a linear strain gauge (Micro-Measurements C2A-06-062LW-350) mounted on the surface of the pellets using a commercial bonding kit (Micro-Measurements MMF006678/M-BOND-200), and the data were acquired through a DAQ device (Micro-Measurements MM01-350) with a built-in Wheatstone quarter-bridge circuit. The magnetic properties of the samples were characterized using a LakeShore (model 735) vibrating sample magnetometer (VSM). All the magnetic measurements were conducted in a transversal (field lines perpendicular to the plane of the pellet) configuration at ambient temperature. The crystal structure of the composites was studied using a Rigaku Smartlab x-ray diffractometer with Cu- α radiation ($\lambda = 1.54060 \text{ \AA}$). The data were collected in the range of $20 < 2\theta < 80$ with a step size of 0.01° and a scan step time of 1 s and analyzed using X'Pert HighScore software.

RESULTS AND DISCUSSION

Two factors play a crucial role in the effectiveness of the ferroic phase conjugation: resistivity of the ceramic, which directly governs the electrical poling effectiveness, and the interface of the two materials, which influences the strain transfer.³⁶ As discussed above, the CoFe_2O_4 pellets were conditioned prior to the measurements through electric poling to optimize ME properties. Due to the finite resistivity of the CoFe_2O_4 phase in the composite and the leakage currents through a network of electrically interconnected

CoFe_2O_4 grains, there are limitations on the magnitude of the electric field that can be applied across the pellet. The dependence of the maximum achievable electric field that was applied during the poling (before samples get damaged by local Joule heating) and the corresponding resistivity values of the samples at the poling temperature (150°C , see above) on CoFe_2O_4 content and the type of BaTiO_3 precursor (cubic or tetragonal) are shown in Fig. 2(a). Since BaTiO_3 is an insulator, higher BaTiO_3 content leads to better electrical isolation of CoFe_2O_4 grains and the increase in pellet resistance, which, in turn, enables higher poling voltages. To measure the maximum achievable ME coefficient value for a given composition of the composite, the maximum achievable electric field was applied to each sample during electric poling. Furthermore, the values of the ME coefficient resulting from poling under identical conditions were compared. For these measurements, an electric field of 0.8 kV/cm was used, which is the maximum achievable electric field for the composite with the lowest resistivity (using the cubic BaTiO_3 precursor). The ME response as a function of dc magnetic field for $x\text{-CoFe}_2\text{O}_4\text{-(1-x)-BaTiO}_3$ composites prepared with two different types of BaTiO_3 precursors and poled with the highest dc voltage applicable depending on their resistivity is shown in Figs. 2(b) and 2(c). All the curves exhibit hysteretic behavior^{10,28} that originates from the hysteretic nature of the magnetization reversal in CoFe_2O_4 . A comparison of the maximum ME coefficient of the pellets prepared and conditioned differently is shown in Fig. 2(d). The cubic samples produce higher ME coefficients than the

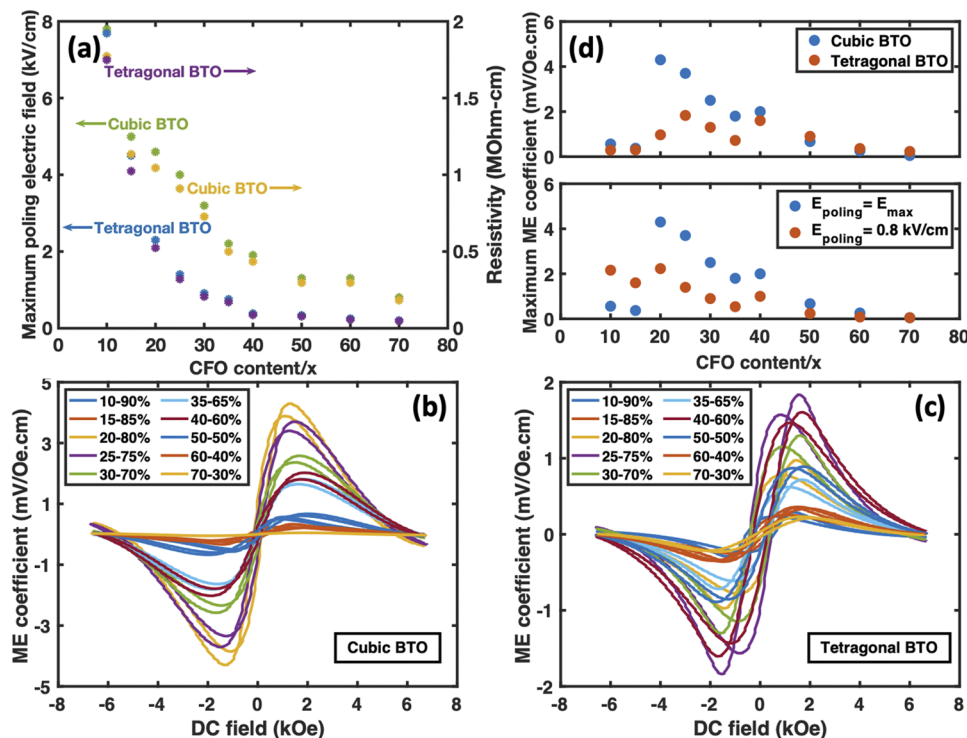


FIG. 2. (a) Correlation of maximum poling electric field and resistivity with CoFe_2O_4 content in CoFe_2O_4 composites, ME coefficient as a function of dc magnetic field for different compositions prepared with (b) cubic and (c) tetragonal BaTiO_3 precursors, (d) maximum ME coefficient vs CoFe_2O_4 content in different composites depending on the BaTiO_3 precursor type (top) and magnitude of the poling electric field applied to cubic samples (bottom).

tetragonal samples when the concentration of CoFe_2O_4 is below 50%. The highest ME coefficient is achieved at a CoFe_2O_4 : BaTiO_3 concentration of 20%–80% for cubic samples (4.3 mV/Oe cm) and 25%–75% for tetragonal samples (1.83 mV/Oe cm). When the samples based on cubic BaTiO_3 precursor were poled at the same electric fields (0.8 kV/cm), the ME coefficient of each composite is reduced, but their relative performance remains approximately the same. The samples were prepared multiple times to verify these trends.

Piezo-Force Microscopy (PFM) images of $0.3\text{CoFe}_2\text{O}_4$ – 0.7BaTiO_3 composites are shown in Fig. 3. These samples were polished to a mirror finish (rms roughness below 10 nm) using progressively higher grit sandpaper followed by polishing paste. The PFM probe is placed in contact with the sample surface. Upon applying a 5 V ac driving voltage to the probe, the piezoelectric domains in the sample respond by straining, which leads to the deflection of the cantilever. This deflection is interpreted as piezo-amplitude and piezo-phase images that exhibit a contrast between piezoelectric BaTiO_3 and non-piezoelectric CoFe_2O_4 materials. The images show CoFe_2O_4 grains (darker regions on PFM amplitude and phase scans) within a BaTiO_3 matrix (lighter regions), as the brighter domains have higher piezoresponse and a different phase compared to dark regions. The variations in the PFM amplitude observed for BaTiO_3 grains result from the variations of crystallographic orientation of individual grains with respect to the excitation electric field, properties of surrounding grains, individual grain sizes, residual stresses, etc. The characteristic grain sizes observed in the sample prepared using cubic BaTiO_3 powder are significantly larger than the grain sizes in the sample prepared using tetragonal BaTiO_3 powder [see Figs. 3(b) and 3(e)], which is the result of significant differences in the morphologies and

compositions of BaTiO_3 / CoFe_2O_4 precursor mixtures that affect the grain growth dynamics.^{37–41}

Due to the better isolation of CoFe_2O_4 grains in cubic samples compared to the networked CoFe_2O_4 grains in tetragonal ones, they can be poled more efficiently. Moreover, the formation of a higher interfacial area or core-shell-like structure between piezomagnetic and piezoelectric phases in samples prepared with cubic BaTiO_3 precursor facilitates the strain transfer between two phases.

SEM images of $0.3\text{CoFe}_2\text{O}_4$ – 0.7BaTiO_3 samples for the cases of cubic and tetragonal BaTiO_3 precursors are shown in Figs. 4(a) and 4(b), respectively. To distinguish between CoFe_2O_4 and BaTiO_3 phases, the samples were etched in hydrochloric acid (HCl 50% v/v aqueous solution) for 3 h to selectively remove CoFe_2O_4 . The resulting SEM images of HCl etched $0.3\text{CoFe}_2\text{O}_4$ – 0.7BaTiO_3 samples for the cases of cubic and tetragonal BaTiO_3 precursors are shown in Figs. 4(b) and 4(e), respectively. Focused ion-beam (FIB) cross-sectioning was used to reveal the depth profile of the composite microstructure. It should be noted that material damage due to Ga ion implantation during typical FIB cross-sectioning used in this work is limited to ~ 20 nm penetration depth, which is significantly smaller than the characteristic length scales probed here.⁴² As shown in Fig. 4(f), the voids (dissolved CoFe_2O_4) in the samples based on tetragonal BaTiO_3 precursors extend up to $8\text{ }\mu\text{m}$ below the surface of the sample. Since the pores (etched away CoFe_2O_4) are observed all the way down to $8\text{ }\mu\text{m}$ below the surface, CoFe_2O_4 grains in the tetragonal BaTiO_3 precursor based samples are fairly well interconnected. On the other hand, the FIB cross section of the sample based on cubic BaTiO_3 precursor reveals that individual CoFe_2O_4 grains are physically isolated from each other (by BaTiO_3) since no voids are observed below the sample surface [see Fig. 4(c)]. This is

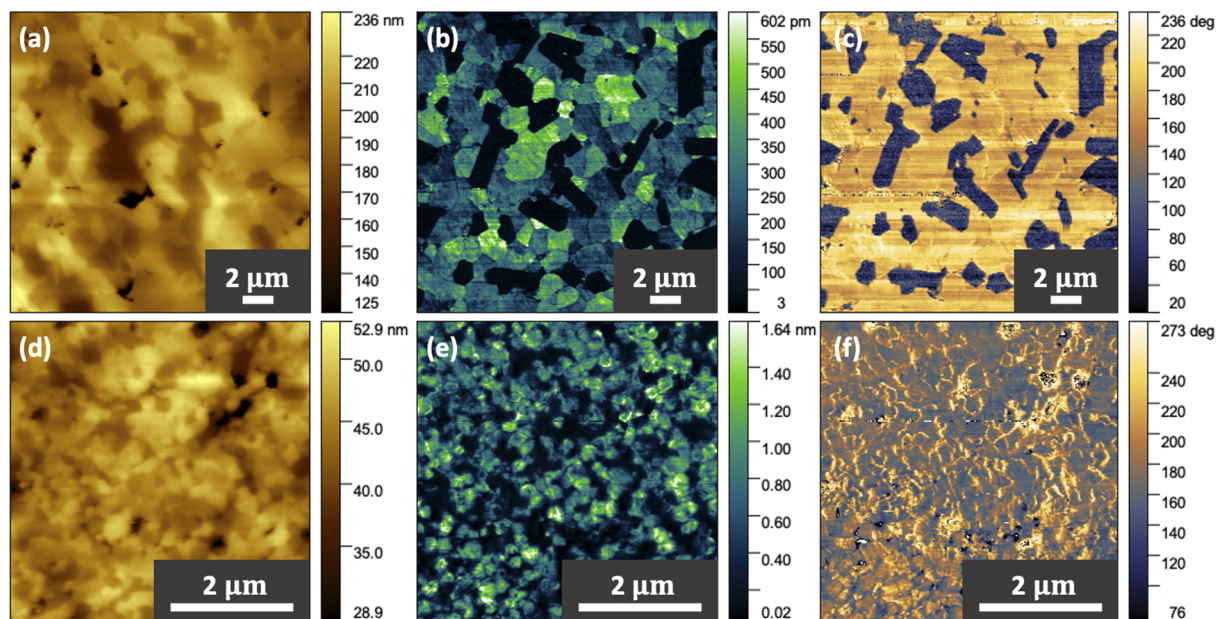


FIG. 3. PFM imaging of $0.3\text{CoFe}_2\text{O}_4$ – 0.7BaTiO_3 composites prepared with cubic (top row) and tetragonal (bottom row) BaTiO_3 precursors: [(a) and (d)] height (surface topography), [(b) and (e)] PFM amplitude, and [(c) and (f)] PFM phase.

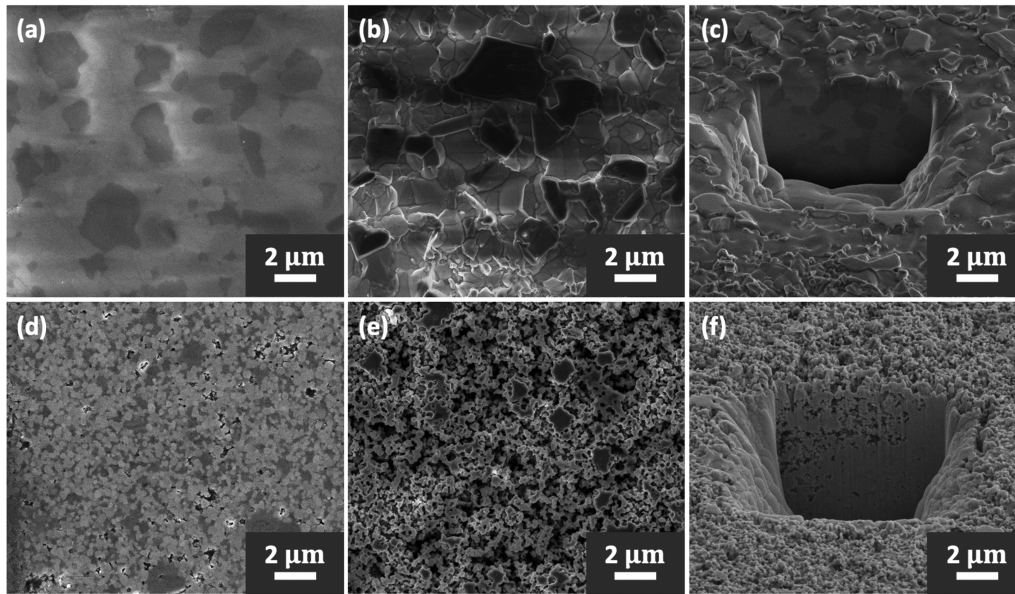


FIG. 4. SEM images of polished 0.3CoFe₂O₄–0.7BaTiO₃ composites (cubic: top and tetragonal BaTiO₃: bottom row): [(a) and (d)] surface, [(b) and (e)] etched surface, and [(c) and (f)] FIB-etched cross section.

in agreement with lower resistance observed in tetragonal precursor samples as compared to cubic ones.

The dependence of magnetostriction, λ , and piezomagnetic coefficient, $d\lambda/dH$, on the magnitude of applied dc magnetic field

for 0.3CoFe₂O₄–0.7BaTiO₃ composite prepared with two types of BaTiO₃ is shown in Figs. 5(a) and 5(b), respectively. The composite synthesized with the cubic BaTiO₃ precursor exhibits lower magnetostriction values compared to the tetragonal BaTiO₃ precursor

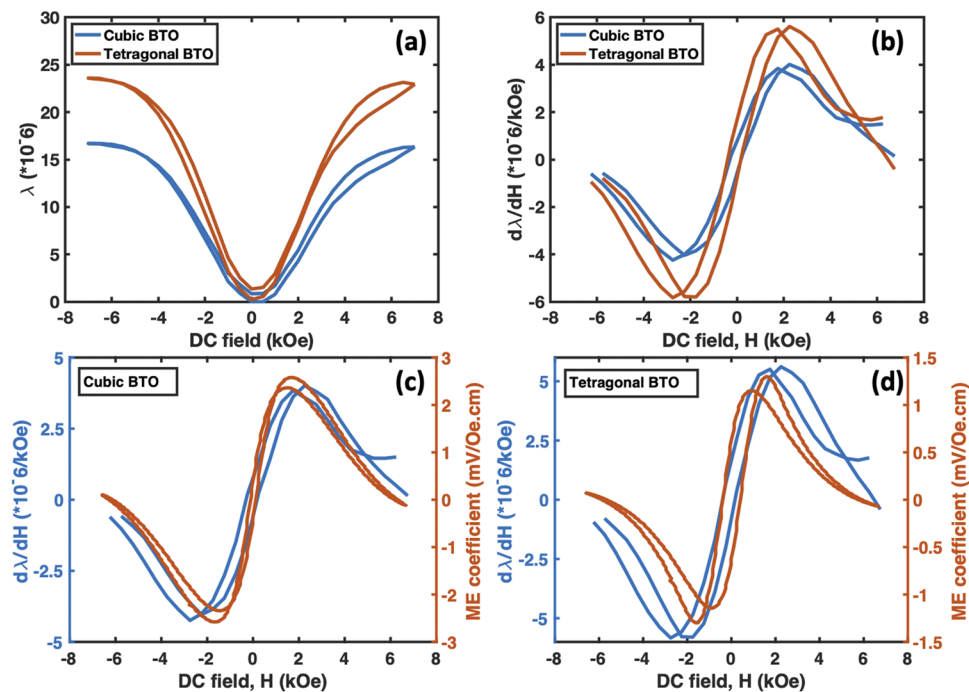


FIG. 5. (a) Comparison of magnetostriction, λ , as a function of DC magnetic field in 0.3CoFe₂O₄–0.7BaTiO₃ composites, (b) comparison of the derivative of magnetostriction, and [(c) and (d)] comparison of the derivative of magnetostriction and ME coefficient for cubic and tetragonal composites, respectively.

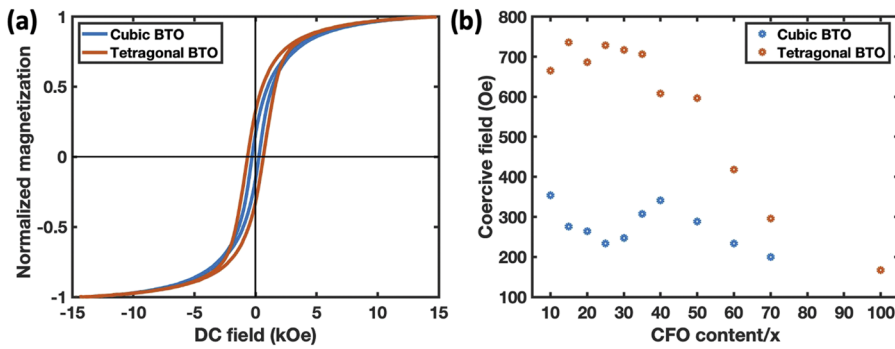


FIG. 6. (a) M-H loop of 0.3CoFe₂O₄-0.7BaTiO₃ composites and (b) variation of coercivity with CoFe₂O₄ proportion in the composite.

based samples. This is attributed to the finer microstructure and smaller CoFe₂O₄ grain sizes in tetragonal BaTiO₃ samples that help to more effectively distribute the strain throughout the composite.¹⁸ It should be noted that the coercivity values are the same in the magnetic field dependencies of the ME coefficient, magnetostriction, and magnetization (see Fig. 6).^{43,44}

The dependence of the magnetoelectric coefficient on several materials properties can be approximately described using the following equation:⁴⁵

$$\alpha_{ME} = x(1-x) \cdot \frac{d\lambda}{dH} \cdot \frac{d_{33}}{\epsilon_{r33}} \cdot Y_{33}, \quad (1)$$

where x is the volume fraction of the magnetostrictive component, $d\lambda/dH$ is the piezomagnetic coefficient, d_{33} is the piezoelectric

coefficient, ϵ_{r33} is the relative permittivity of the composite, and Y_{33} is Young's modulus. The above equation is a relatively crude approximation; however, it aids in the interpretation of the trends observed in experimental data. According to Eq. (1), the magnetoelectric coefficient, α_{ME} , is proportional to the value of piezomagnetic coefficient, $d\lambda/dH$, at a given dc magnetic field, which is consistent with the respective data shown in Figs. 5(c) and 5(d).^{32,34} Although the piezomagnetic coefficient is higher for CoFe₂O₄-BaTiO₃ composites based on the tetragonal BaTiO₃ precursor, it does not result in higher magnetoelectric coefficient values, as shown in Fig. 2. The value of the magnetoelectric coefficient is affected by a higher dielectric constant due to the lower resistivity of tetragonal BaTiO₃ based composites [see Eq. (1)], limitations to effectively pole the composites (again due to low resistivity),

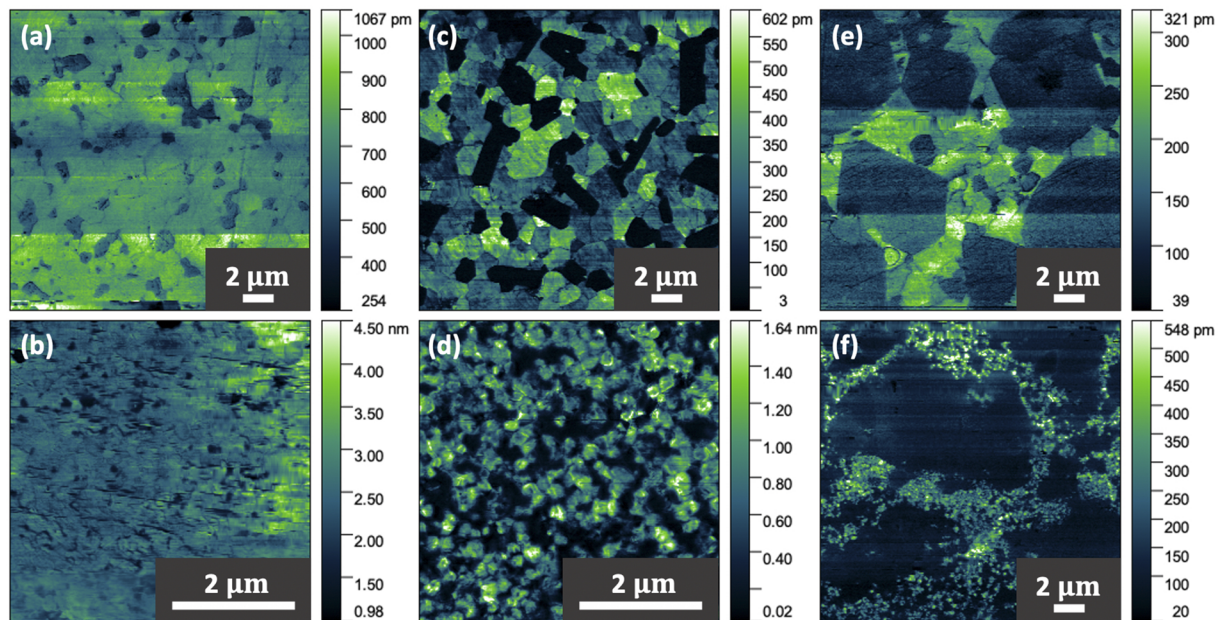


FIG. 7. Comparison of PFM amplitude scans of CoFe₂O₄-BaTiO₃ composites prepared with cubic (top row) and tetragonal (bottom row) BaTiO₃ precursors for CoFe₂O₄-BaTiO₃ composites: [(a) and (b)] 10%-90%, [(c) and (d)] 30%-70%, and [(e) and (f)] 70%-30%.

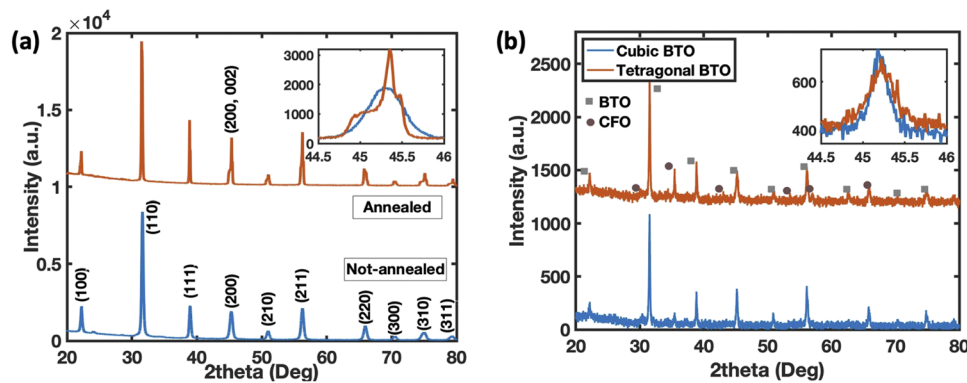


FIG. 8. X-ray diffraction patterns of (a) cubic BaTiO₃ before and after annealing at 1200 °C and (b) annealed 0.3CoFe₂O₄–0.7BaTiO₃ composites. The inset shows the BaTiO₃ (200) reflection.

and a variety of other factors including significant microstructural differences.

The M–H loops for 0.3CoFe₂O₄–0.7BaTiO₃ composites and the dependence of their coercivity on CoFe₂O₄ content are shown in Figs. 6(a) and 6(b), respectively. The magnetic field was applied perpendicular to the pellet surface. The observation of the lower coercivity values in samples prepared using the cubic BaTiO₃ precursor is consistent with the above observation that CoFe₂O₄ grain size in these samples is significantly larger than CoFe₂O₄ grain size in samples prepared using the tetragonal BaTiO₃ precursor. The large CoFe₂O₄ grain size (>1 μm) facilitates magnetization reversal processes via domain wall motion resulting in lower coercivity values.

PFM amplitude scans shown in Fig. 7 for samples prepared cubic and tetragonal BaTiO₃ precursors illustrate the increase in the characteristic CoFe₂O₄ grain sizes [dark regions with zero (or near zero) PFM amplitude correspond to CoFe₂O₄ grains] with the increase in CoFe₂O₄ content in the CoFe₂O₄–BaTiO₃ composite. Similarly to the above observations of coercivity value differences between samples prepared cubic and tetragonal BaTiO₃ precursors, the increase in CoFe₂O₄ grain size for higher CoFe₂O₄ content samples leads to the reduction of the composite coercivity. This is also consistent with previously published reports.^{46–48}

The XRD spectra of cubic BaTiO₃ before and after annealing at 1200 °C for 4 h are shown in Fig. 8(a). Non-annealed cubic BaTiO₃ holds Pm-3m space group (JCPDS data No.: 01-074-1961) with the calculated lattice parameters of $a = b = c = 3.9966$ Å.^{49–51} While characteristic peaks of tetragonal BaTiO₃ are observed for the annealed powder and indexed with P4mm space group (JCPDS No.: 01-081-2201) with lattice parameters of $a = b = 3.9961$ Å and $c = 4.03219$ Å. The estimated tetragonality factor (c/a) is 1.009, which is close to the bulk value of 1.011. The XRD spectra of 0.3CoFe₂O₄–0.7BaTiO₃ samples after annealing are shown in Fig. 8(b). The two patterns do not exhibit peak splitting at 45° corresponding to the Miller index of (200) and (002) as expected for the tetragonal crystal structure. This can be attributed to the peak broadening of nano-crystalline particles or the cubic-dominant structure, which leads to the lower tetragonality factor.^{52,53} However, as demonstrated in this work, the

composite samples based on both cubic and tetragonal precursors do exhibit magnetoelectric properties, which confirms the presence of tetragonal BaTiO₃ in the composite.

CONCLUSIONS

In summary, magnetoelectric composites of CoFe₂O₄–BaTiO₃ were synthesized using commercial CoFe₂O₄ and BaTiO₃ precursors and an inexpensive and scalable process based on ball-milling and high-temperature sintering/annealing. It was observed that magnetoelectric properties are strongly affected by the CoFe₂O₄–BaTiO₃ composition, where the highest magnetoelectric coefficient is exhibited in samples prepared from a 20% CoFe₂O₄/80% BaTiO₃ precursor mixture. The effect of size and crystal structure of the BaTiO₃ nanoparticle precursor on magnetoelectric and related magnetic properties of the CoFe₂O₄–BaTiO₃ composite was investigated. Higher magnetoelectric coupling coefficients comparable to those of core-shell nanostructures were observed for composites prepared with 50 nm cubic BaTiO₃. Microstructural characterization using SEM and PFM revealed that CoFe₂O₄ grains in a composite based on cubic BaTiO₃ precursor nanoparticles are larger and better isolated from each other by the surrounding BaTiO₃ matrix than CoFe₂O₄ grains in a composite based on tetragonal BaTiO₃ precursor nanoparticles. Larger, higher crystallinity magnetostrictive (CoFe₂O₄) and piezoelectric (BaTiO₃) phases likely result in enhanced magnetostrictive and piezoelectric coefficients; the enhanced interfaces between the phases improve the coupling between the phases; and higher electrical resistivity enables more effective poling and leads to the effective reduction of the relative permittivity. Combining these effects results in higher ME coefficient values that are observed in the optimized composite based on cubic BaTiO₃ powders.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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